Beyond radiocarbon's "black hole"

^{14}C dating samples older than 40,000 yrs

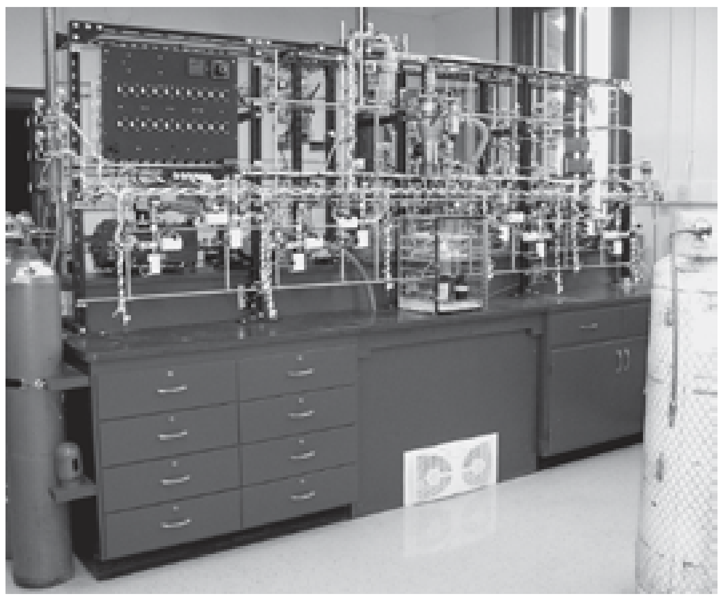
By Jeff Pigati

For Quaternary geologists, the short half-life of ^{14}C (5,730 years) is both a blessing and a curse. While it allows for relatively precise dating of fossil carbon throughout the Holocene and late Pleistocene (the blessing part), those of us interested in looking at events that occurred before ~40,000 years ago must turn elsewhere for chronologic control. Simply put, too few of the original ^{14}C atoms remain after 40 millennia of decay to yield reliable results (the curse). At the Desert Laboratory, we have recently constructed a dedicated vacuum extraction system, which we call "the low-level line," and are refining new chemical pretreatment protocols aimed at thoroughly removing secondary carbon. Together, these advances may allow us to push back the upper limit of ^{14}C dating to as much as 55,000 years ago and perhaps beyond.

First measured shortly after World War II by Willard Libby and his students at the University of Chicago, radiocarbon has revolutionized our understanding of the timing and synchroneity (or lack thereof) of a myriad of climatic, geologic, and anthropologic events over the last 40,000 years. Dubbed "the mother of all isotopes," ^{14}C can be used to determine the age of any material, organic or inorganic, that contains carbon provided that two criteria are met: (1) original carbon atoms can be isolated from the sample material (i.e., all contaminants can be removed), and (2) modern carbon is not introduced at any time during the extraction process. While these criteria are satisfactorily met for Holocene- and late Pleistocene-age material, the impact of contamination increases exponentially with age.

For example, a 10,000-year-old sample that contains 1% modern carbon would yield an age of 9,730 yrs, representing an error of only 270 years. In contrast, the same amount of contamination in a 50,000 year-old sample would result in an apparent age of 35,500 years, a difference of 14,500 years! In fact, older samples that contain small amounts of contamination yield ^{14}C ages that fall between 35,000 and 40,000 years B.P. with such regularity that we refer to this time period as "the black hole" of radiocarbon dating. The implications for ^{14}C dating in and beyond the black hole are clear: even a tiny amount of contamination, whether originally incorporated in the sample material or introduced during the measurement process, can be fatal for old samples.

Our experimental design is based largely on the work of Michael Bird and colleagues at Australia National University in Canberra, as well as on our own experience with measuring low concentrations of cosmogenic ^{14}C in silicate minerals (low, as in part per quintillion!). For organic materials, such as charcoal, samples are initially treated using dilute acids and bases in order to remove the bulk of the secondary carbon species. These steps, followed by a final rinse in dilute acid, are usually sufficient for younger samples and comprise the traditional acid-base-acid (or ABA) treatment that has been used for decades. Our treatment of old charcoal samples begins with the same acid and base steps, but includes a subsequent step in which the base-insoluble fraction is immersed in an oxidizing solution ($K_2Cr_2O_7$ in 2M H_2SO_4) for up to 24 hours. During this step, all carbon species except elemental carbon are oxidized and removed.



The low-level ^{14}C extraction system at the Desert Laboratory located on Tumamoc Hill.

Carbon residue that survives the acid-base-oxidation (or ABOX) treatment is then transferred to the low-level line and subjected to stepped combustion. The idea behind stepped combustion is that labile carbon species, including contaminants that survive the ABOX treatment, typically evolve at lower temperatures (<425°C), whereas elemental carbon evolves at higher temperatures (>550°C). Thus, we simply discard the low-temperature aliquots and use the higher-temperature aliquots for dating.

Based on Bird's results, the ABOX-stepped-combustion (or ABOX-SC) treatment appears to have pushed back the limits of ^{14}C dating to at least 50,000 years ago. It has been used successfully for dating old charcoal from several archeological sites in Australia, as well as charcoal recovered from cave sediments that contained the recently discovered remains of Flores Man (*Homo floresiensis*), the tiny hominids that lived in the caves of Indonesia during the last glacial maximum. Our low-level line incorporates features above and beyond those found in the ANU system, including a backing line through which all atmospheric ^{14}C is removed, chemical scrubbing capabilities, and other technology used for isolating CO2 that we developed as part of our cosmogenic ^{14}C research.

We hope that these technologies and close attention to detail will allow us to reliably measure even older samples. Although we are only at the beginning of our testing process, results thus far have been encouraging. Background levels for the low-level line are at least a factor of three lower than typical blank levels and, with some additional tweaking of our extraction procedures, we may be able to achieve even lower levels.

Once the testing phase is completed (our target is December 2005), we will begin to address the long-standing controversy of when Neanderthals were replaced by modern humans in Europe and Asia. A substantial portion of the chronology at several key sites is based on ^{14}C dates that fall – you guessed it – within radiocarbon's black hole. Are those ages real, or are they artifacts of contamination? Time will tell.